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Catalytic carbonization of wood charcoal: graphite or diamond?

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Abstract

We report on the process of making graphite out of wood by catalytic carbonization. Two different types of microstructure were observed. One type being typical for graphitization of wood without the effect of a catalyst, the main characteristic being the typical fibrillar microstructure related back to the original cellulose morphology. A strong {0 0 0 2} inner diffraction ring corresponding to the 0.336 nm lattice spacing of graphite dominates its diffraction pattern. The other type being typical for graphitization of wood with aluminum as catalyst, the main characteristic being the large sheets of carbon forced upon by the formation of plate like Al_4C_3. This compound is formed as an intermediate reaction product, which dissociates into aluminum vapour and solid carbon. The diffraction pattern indicates a differently textured structure. EELS measurements in the areas of catalytic graphitization indicate a significant decrease of the sp^2 bonding typical for graphite. It can be an indication of the presence of metastable diamond. This diamond-like structure is extremely unstable under influence of the electron beam. It decomposed within 250 s of beam exposure.

Keywords: A. Charcoal; B. Carbonization; Graphitization; C. Transmission electron microscopy (TEM)

1. Introduction

In a recent paper Banhart [1] discusses the stability of diamond under the influence of an electron beam. The most stable configuration of carbon at ambient temperature and pressure is graphite with an energy difference of ~0.02 eV per atom over diamond [2,3]. Due to the high energetic barrier between the two phases, the transition from diamond to graphite at normal conditions is very slow. In a certain temperature window and with a beam voltage above a characteristic accelerating voltage of 100 kV, diamond is more stable than graphite, but exposure at room temperature does transform the diamond back into graphite again [1]. The recent interest in diamond with respect to device technology [4] and in diamond-like coatings for tribological applications [5] makes these findings of crucial importance, as the dimensions are of nano scale and transmission electron microscopy (TEM) is the method of choice. We have studied catalytic carbonization of wood charcoal using Al-triisopropoxide as a catalyst. Related research on diamond formation by subtracting the metal out of metal silicides are given by Gogotsi and co-workers [6] for SiC and TiC, respectively.

2. Experimental

Sugi (*Cryptomeria japonica*) wood choppings were preheated at 500 °C for 1 h. The temperature was increased by 4 °C/min in argon. The wood charcoal was pulverized and subsequently soaked in a 40% isopropyl alcohol solution of Al-triisopropoxide. After soaking for 24 h, the specimen was dried at 105 °C for 24 h, sieved with a 1.27 mesh size pass, and graphitized in a direct pulse-heating device (Plasman, S S Alloy, Hiroshima, Nishimiya [7]). The major advantage of this apparatus is that the electric pulsing and the pressure are applied directly to the specimen powder inside the die. The weight percentage of aluminum was 10% based on the weight of dry wood charcoal. The graphitizing temperature was 2200 °C, the reaction time was 5 min and the

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pressure was 50 MPa. Samples were analyzed in an analytical JEM 2010F electron microscope equipped with a Gatan Imaging Filter at 200 kV.

3. Results and discussion

Given a heat treatment of 5 min at 2200 °C graphitization of wood charcoal already takes place by itself producing microfibrils based on the original cellulose morphology. This is notably different from the case in which Al is added. If present Al reacts with the carbon to form, as an intermediate, a plate like Al_4C_3 phase, which, subsequently dissociates in Al vapor and sheets of solid carbon [8]. Correspondingly, two types of microstructures could be expected. The first one being represented on Fig. 1(a) illustrating randomly oriented graphitic microfibrils. The selected area diffraction pattern (SADP) shown in Fig. 1(b) reveals a strong, inner ring corresponding to the graphite lattice spacing of $d_{0002} = 0.336$ nm. The HRTEM image of the same graphitized area is given in Fig. 1(c). One easily finds such micrographs in the sample, implying substantial graphitization without the intermediate Al-phase. However, in the same sample we frequently observed a rather different structure as on Fig. 2 caused by the catalytic process. The Al addition forces the carbon to react to Al_4C_3, a hexagonal structure with space group $P6_3mc$ (186), which grows along the basal plane with the $\langle 1\,1\,-2\,0\rangle$ as plane normal. These plates dissociate and produce clearly textured graphite. Its SADP in Fig. 2(b) shows an inner diffraction ring, which is slightly elliptic. It shows $\{1\,0\,-1\,0\}$ planes in northwesterly and $\{1\,0\,-1\,1\}$ planes in northeasterly direction; the second also elliptic ring shows $\{1\,1\,-2\,0\}$ planes in northwesterly and $\{1\,1\,-2\,2\}$ planes in northeasterly direction. It is clear evidence of the textured graphite. Zooming in on such an area a crystalline structure is present (Fig. 2(c))

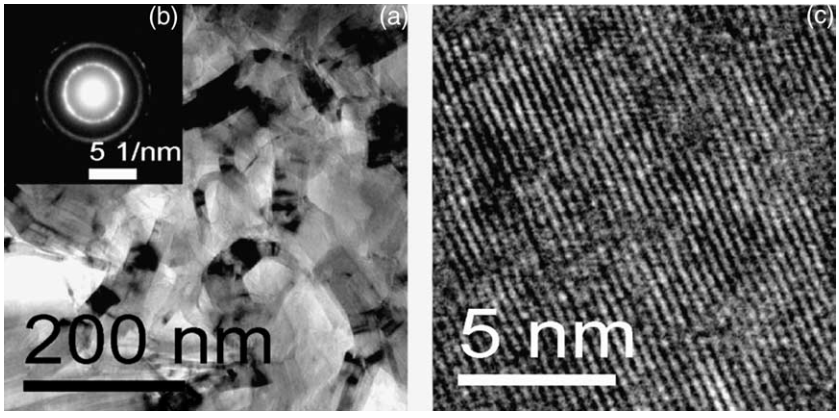

Fig. 1. (a) Bright field TEM image showing fibrillar graphite. (b) Inset: corresponding diffraction pattern. The inner ring represents the (0 0 0 2) of graphite with an 0.336 nm lattice spacing. The other much fainter rings are the ones explained in the caption of Fig. 2 passing the aperture as well. (c) HRTEM image of one of the fibrils with 0.336 nm between basal planes.

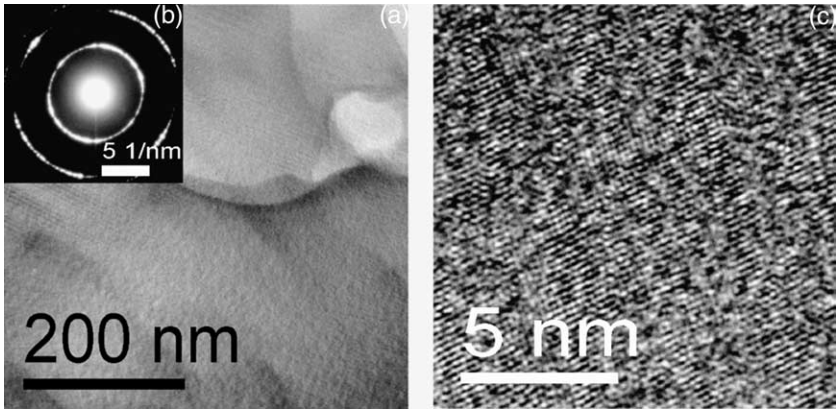

Fig. 2. (a) Bright field TEM image of an area where catalytic graphitization took place. (b) Inset: corresponding diffraction pattern. The inner, slightly elliptic ring represents the d spacings of graphite with 0.213 nm for the (1 0 −1 0) and 0.203 nm for the (1 0 −1 1). The outer strongly textured set of rings represent also d spacings of graphite with 0.107 nm for the (1 1 −2 0) and 0.102 nm for the (1 1 −2 2). (c) HRTEM image of the low index planes of graphite overlapping the possible {1 1 1} planes of metastable diamond-with 0.206 nm as lattice spacing.

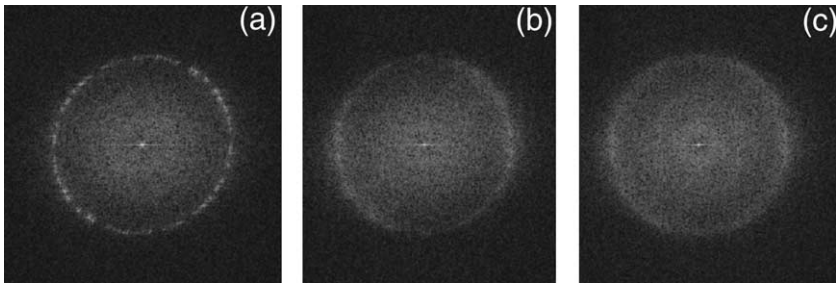

Fig. 3. (a) FFT image with the ring representing the {1 1 1} spacings of diamond as imaged in Fig. 2(c), taken immediately after the first exposure to the electron beam. (b) FFT image corresponding to Fig. 2(c), taken 125 s after the first exposure to the electron beam. (c) FFT image corresponding to Fig. 2(c), taken 250 s after the first exposure to the electron beam.

of which its FFT (Fig. 3(a)) shows a similar elliptic effect as in the case of SAD. EELS measurements of the same area (Fig. 4) reveal a significant reduction of the sp^2 bonding typical for the areas of non-catalytic graphitization. This may indicate the presence of a metastable diamond-like structure. A similar behavior of small diamond patches was already reported earlier [9]. Such structure was decomposed very rapidly during exposure to the electron beam. The FFT of the HRTEM pictures shown on Fig. 3 with the ring representing the {1 1 1} planes in diamond reveal the rapid decomposition of the structure.

In order to make this finding a bit more quantitative, we made the following calculation. We first determined the area in Fig. 2(c) as being 17.067 nm^2. Then we checked our notebook for the electron dose during the sequence from the first FFT up to the last FFT, a period of 250 s, and found a value of 330 pA/cm^2. This means a total number of 200 keV electrons, as follows:

$$\begin{aligned}\#\text{electrons} &= (330 \times 10^{-20})\ \text{C nm}^{-2}\,\text{s}^{-1} \times (17.067)\ \text{nm}^2 \\ &\quad \times 250\ \text{s} \times (1.6 \times 10^{-19})^{-1}\ \text{C}^{-1} \\ &= 8.8 \times 10^4\ \text{electrons} \qquad (1)\end{aligned}$$

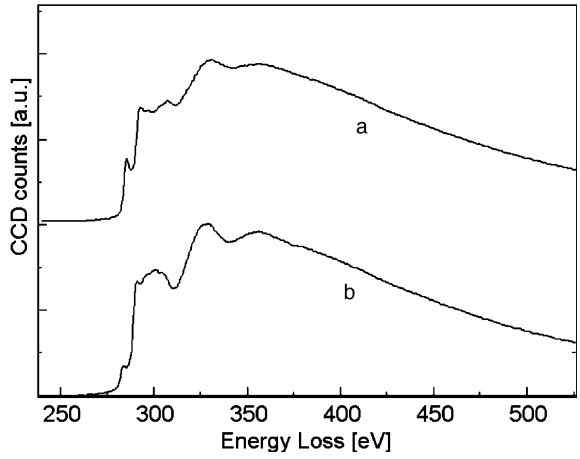

Fig. 4. Two EELS spectra showing the difference in initial peak representing the sp^2 bonding in the area containing graphite produced by non-catalytic graphitization (a) and where catalytic graphitization took place (b).

If we take the atom density as being 1 carbon atom per 0.04 nm^2, we effectively irradiated $17.067/0.04 = 427$ atoms with 206 electrons per atom of 200 kV energy. To avoid this effect, one should try to keep electron dose and exposure time as low as possible, or, even better, work with accelerating voltages below 100 kV [1].

4. Conclusion

Wood charcoal graphitized by thermal heating at 2200 °C for 5 min is dominated by a microfibrillar pattern related to the original cellulose morphology. By mixing wood charcoal with Al-triisopropoxide the intermediate Al_4C_3 phase is formed, which crystallizes in large plates and, in a certain temperature window, even dissociates into Al vapour and graphene sheets having strong texture. These sheets contain a certain amount of diamond-like structure as was shown by EELS measurements. This diamond like structure, which was formed at high temperature, is decomposed at ambient temperature during exposure to the 200 kV electron beam within 250 s [1].

Acknowledgements

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